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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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Novel Small -Ring -Compounds of Phosphorus: Azaphosphaborirenes, Diphosphadiboretanes and Azaphosphadiboretidines

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To cite this Article Kölle, Peter and Nöth, Heinrich(1987) 'Novel Small -Ring -Compounds of Phosphorus: Azaphosphaborirenes, Diphosphadiboretanes and Azaphosphadiboretidines', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 30: 1, 475 — 478

To link to this Article: DOI: 10.1080/03086648708080623

URL: <http://dx.doi.org/10.1080/03086648708080623>

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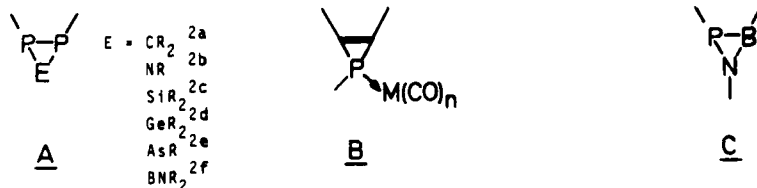
NOVEL SMALL-RING-COMPOUNDS OF PHOSPHORUS:
AZAPHOSPHABORIRENES, DIPHOSPHADIBORETANES AND
AZAPHOSPHADIBORETIDINES

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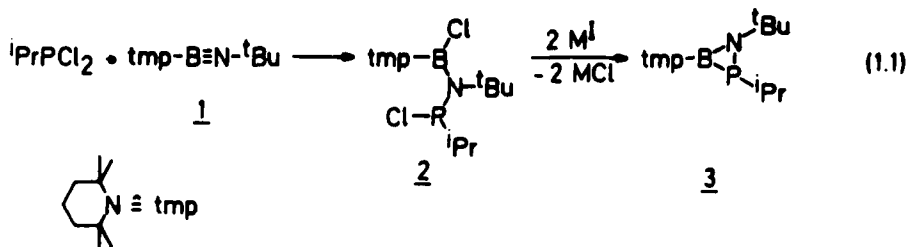
Abstract Synthesis, physical data and the structure of the title ring compounds are discussed, and in addition 1.4.2.3.5.6-diphosphatetetraborinanes. They exhibit various degrees of thermal stability and show some unusual features in the reaction with sulfur and selenium

A number of small ring compounds of phosphorus, such as cyclotri- and cyclo-tetraphosphanes ¹ and diphosphiranes A have been reported ².



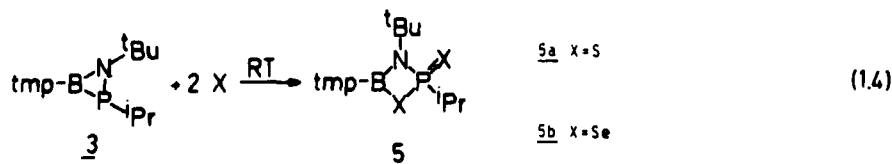
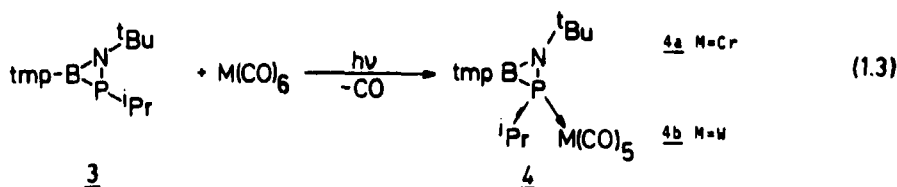
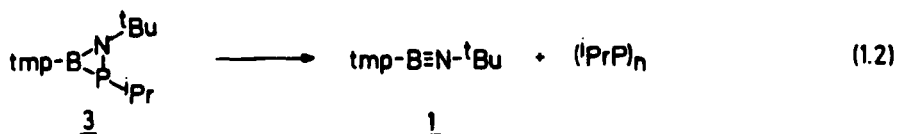
A phosphirene B was considered to be unstable but F. MATHEY et. al. have stabilized this unsaturated PC₂-ring-system as a ligand ³; shortly thereafter the free ligand became accessible ⁴.

In view of the isoelectronic relationship between a carbon-carbon- and a boron-nitrogen bond, we attempted the synthesis of derivatives of the three membered azaphosphaborirene C. Reaction (1.1) gives access to the derivative 3, characterized by a highly shielded ³¹P-atom (δ³¹P: -92) and its molecular weight.

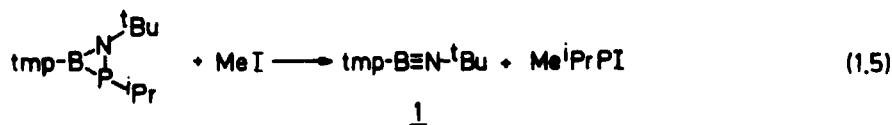


The compound 3 proved to be highly reactive.

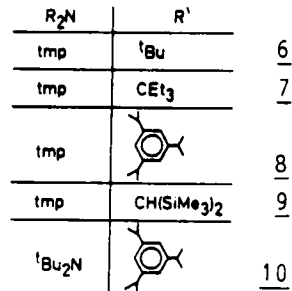
- i) it decomposes thermally to the aminoiminoborane $\text{tmpB}=\text{NCMe}_3$ 1 and cyclopolyphosphanes (reaction 1.2)
- ii) it behaves as a two electron donor to metal carbonyl fragments (reaction 1.3) and
- iii) it reacts with sulfur and selenium to provide ring expansion products (reaction 1.4)



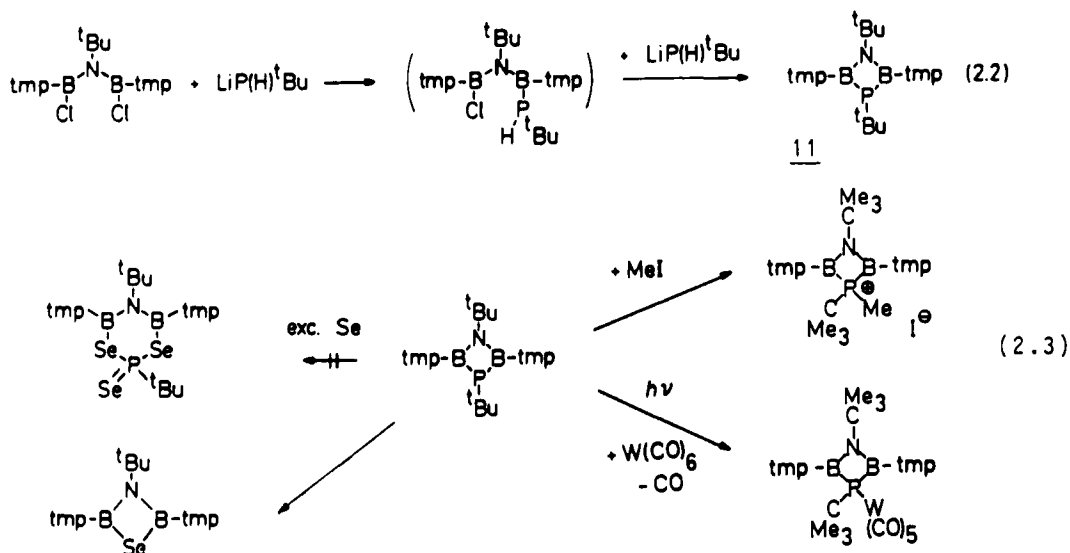
3 reacts also with CH_3I , however not with the expected phosphonium-salt formation, but surprisingly, by ring cleavage as shown in reaction (1.5)



Our attempts to synthesize the "two-membered" boraphosphene $\text{R}_2\text{NB}=\text{PR}$; containing a boron-phosphorus double-bond have so far lead only to a number of its dimers, the 1.3.2.4-diphosphadiboretanes 6 - 10 (reaction 2.1)

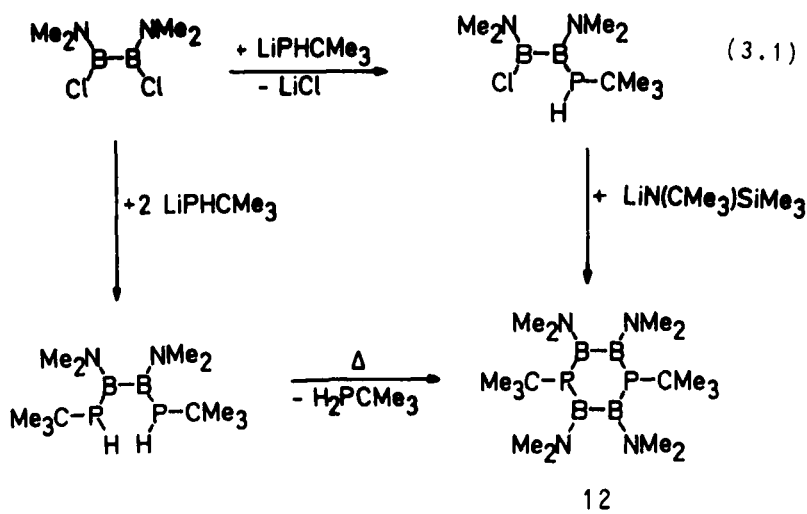


Since 3 readily decomposes with formation of an aminoiminoborane, derivatives of the 1,3,2,4-azaphosphadiboretidine may be expected as sources of boraphosphenes. The derivative 11 was obtained in a multistep synthesis; some steps are described in (2,2).



11 behaves as a phosphane in its reaction with metal-carbonyls, e.g. $W(CO)_6$. More interestingly, selenium removes the phosphorus atom from the ring system as shown in (2.3).

The smallest BP-ring, containing a diboron unit, is a 1.2.3.4-diphosphadiboretan, described in 1985 by M. Baudler ⁵. 3-membered phosphadiboriranes are still unknown. Our attempts to synthesize this ring-systems are shown in (3.1). However, only the new six membered 1.4.2.3.5.6-diphosphatetra-borinan system 12 was obtained and characterized by its X-ray crystal structure.



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